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# ***In situ* formation of onion-like carbon from the evaporation of ultra-dispersed nanodiamonds**

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## **Abstract**

We report the *in-situ* formation of onion-like carbon (OLC) by evaporation from a nanodiamond source under ultra-high vacuum conditions. The OLC is characterized by transmission electron microscopy (TEM), atomic force microscopy (AFM), Raman spectroscopy and X-ray photoelectron spectroscopy (XPS) and is found to be highly defective but completely separated. The absence of any signature in XPS, Raman spectra and TEM associated with nanodiamond in the film suggests that the OLC is formed from carbon vapor or by the direct evaporation of only the smallest particles resulting from nanodiamond graphitization. The method thus provides a route to the formation of individually separated OLC nanoparticles.

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## 1. Introduction

Onion-like carbon clusters are an interesting class of materials that were discovered [1, 2] much earlier than other nano-carbons such as fullerenes and nanotubes. Onion-like carbons possess a wide range of properties, which make them of interest for applications such as lubrication [3] and fuel cells [4]. More recently onion-like carbon has been considered to have potential for use in electrochemical super capacitors [5, 6]. Newly developed routes for the functionalization of onion-like carbon (OLC) nanoparticles with polycyclic aromatic hydrocarbons (anthracene) by direct covalent binding [7] shows that OLCs are worthy of multidisciplinary attention in fields such as environmental science and astronomy.

Carbon onion synthesis can be broadly grouped into two methods: (A) temperature or irradiation induced transformation of other forms of carbon (such as carbon soot [8] or ultra-dispersed diamond [9, 10, 11]) into concentric spherical cages, and (B) those involving continuous segregation of carbon from matrices in which there is low solubility (for example, through carbon ion implantation into Ag and Cu for host matrices [12]).

In this Letter we report the formation and evaporation of separated onion-like carbon particles on a silicon substrate under ultrahigh vacuum (UHV) conditions. X-ray photoemission spectroscopy (XPS), atomic force microscopy (AFM), Raman spectroscopy and high resolution transmission electron microscopy (HRTEM) have been performed to characterize the evaporated onion-like carbon. In particular, we find that the OLC present in the evaporated films originates either from atomic carbon emitted from the nanodiamond source or by evaporation of only the smallest (diameter  $\leq 2$  nm) OLC particles produced by nanodiamond graphitization.

## 2. Experimental section

Carbon onions were produced in an UHV chamber with a base pressure better than  $1 \times 10^{-9}$  mbar using ultra-dispersed nanodiamond as a precursor. Nanodiamond (ND) powders were produced through explosion of a 50:50 TNT/RDX (trityl/cyclotrimethylene-trinitramine) mixture in a hermetic tank and isolated from the detonation soot by oxidative treatment with a mixture of  $\text{HClO}_4$  and  $\text{H}_2\text{SO}_4$  [9-11]. According to small angle X-ray scattering and HRTEM studies, the size of ND particles varied from 2-20 nm, with an average size of 4.7 nm [9, 11]. Nanodiamond powders were heated for 20 mins in a home-made tantalum electron beam evaporator to temperatures between 1400 and 1700K and the evaporated material collected on a substrate (see below) held at room temperature in line-of-sight of the evaporator. The temperature of the tantalum pocket containing the ND was measured using an appropriately calibrated optical pyrometer during heating. Prior to placing the substrate in line-of-sight of the evaporator, the latter was thoroughly outgassed up to the operating temperature, a process which typically took 30 minutes at a pressure of  $5 \times 10^{-9}$  mbar. X-ray photoemission spectroscopy was performed using non-monochromated  $\text{AlK}_\alpha$  radiation (photon energy 1486.6 eV) and a 150 mm hemispherical analyser giving a total instrumental resolution of 0.85 eV *in-situ* on films evaporated onto silicon substrates. HRTEM images were obtained by evaporating material onto a grid coated with oxidized silicon, which was then transferred to a JEOL JEM-2010 microscope operating at beam energy of 200 keV. Atomic Force microscopy (AFM) images were obtained *ex-situ* in tapping mode from material evaporated onto silicon substrates using a Digital Instruments Multimode microscope with a silicon nitride cantilever. Raman spectroscopy was performed *ex-situ* on the silicon-supported films using a Jobin Yvon Confocal Raman Microscope

using an excitation wavelength of 514 nm and an incident power of 20 mW. Typically, five Raman spectra were taken on different regions of each sample to confirm homogeneity over the area of the sample.

### 3. Results and discussion

Fig. 1 shows a HRTEM micrograph of material evaporated directly on to an oxidized silicon-coated microscope grid, demonstrating the presence of OLC particles, the arrows indicate the position of the particles. Close examination of the walls of the OLC particles shows them to be rather discontinuous and rough, which is indicative of a substantial concentration of defects. Previous studies, which examined nanodiamonds annealed under vacuum (without evaporation) for periods of 1 hour [11] showed that for annealing temperatures of 1100 – 1600 K (similar to the evaporator temperatures used in this work) spiral multishell carbon particles are observed with bonding intermediate between  $sp^2$  and  $sp^3$ . These shells surround a residual nano-diamond core, forming a ‘buckydiamond’. The HRTEM image in Fig.1 does not show the presence of nanodiamond cores in the evaporated material, however, the poor contrast, which results from the similar atomic numbers of carbon and the silicon support, means that it is not possible to completely rule out the presence of such structures by this technique.

In order to further investigate the size distribution and separation of the OLC formed through evaporation we performed AFM measurements on silicon samples onto which low coverages of material had been evaporated under the same conditions as the samples prepared for HRTEM. A typical AFM topographic image is shown in Fig. 2 in which individual spherical particles and agglomerates, identifiable as OLC, can be observed. Individual OLC particles are found to have heights in the range

3 - 6 nm, consistent with HRTEM, and the agglomerations are typically 10 – 15 nm in height.

Fig. 3 shows C1s core level photoemission spectra from the evaporated films obtained in two different emission geometries. At normal emission geometry two peaks are readily visible: one at binding energy of  $284.45 \pm 0.05$  eV which corresponds to  $sp^2$  hybridized carbon, as previously determined in a study where OLC was produced directly by annealing nanodiamond particles [11]. The  $sp^2$  component in C1s core-level spectra of the annealed OLC is shifted  $\sim 0.3$  eV to higher binding energy with respect to that for HOPG [13] – this positive shift has been attributed to the large curvature of the graphitic layers of OLC [11]. The shoulder observed at a binding energy of  $282.85 \pm 0.05$  eV is attributed to SiC [14]. We do not see any indication of a component associated with  $sp^3$  bound carbon in the C1s spectra, which indicates an absence of ND in the evaporated material, in agreement with the conclusions drawn from HRTEM. In the more grazing emission geometry (45 degrees) the intensity of the SiC-related shoulder diminishes, demonstrating that this feature is formed at the interface between the film and silicon substrate. There are two possible reasons for the presence of interfacial SiC: individual carbon atoms may evaporate from the tantalum evaporator and chemically bind to the silicon forming silicon carbide; alternatively energetic ('hot') OLC may react with the silicon substrate. A similar phenomenon to the latter scenario has been observed when fullerenes [15, 16] and single wall-carbon nanotubes [17] supported on silicon are annealed at elevated temperatures.

When produced directly by annealing ultra-dispersed nanodiamond, OLC samples show a clear  $\pi$  plasmon loss in the C1s core-level photoelectron spectra

[11, 18], which is notably absent in the spectra shown in Fig. 3. Suppression of plasmon losses [19] and broadening of the C1s core level with respect to ‘pristine’ nano-carbons [20] has been observed in carbon nanotubes damaged by energetic particle irradiation and in nanodiamonds partially graphitized by annealing at 1420 K [11]. The absence of the  $\pi$  plasmon loss in our data may be associated with either a high defect density due to incomplete graphitization or a degradation of  $p$  orbital overlap compared with planar graphite layers due to high curvature of the OLC walls, both of which are compatible with the HRTEM measurements described above.

The Raman spectrum of the evaporated (OLC) material is presented in Fig. 4 and is typical of carbon nanomaterials. It was shown in an earlier Raman study by Obraztsova *et al.* [21], that the Raman spectrum of OLC formed by annealing ND precursors possesses two distinct bands associated with ‘disordered’ carbon ( $D$ ) and ‘graphitic’ carbon ( $G$ ). Sano *et al.* [22], examining OLC formed by arc-discharge under water observed more modes in addition to a  $G$  band frequency much closer to that of HOPG, which implied that onions are perfectly spherical with fewer defects. In our experiment both  $D$  and  $G$  bands are observed (Fig. 4), with similar intensity, at  $1350\text{ cm}^{-1}$  and  $1590\text{ cm}^{-1}$  respectively. The ratio of the intensities of these two bands is often used as a measure of disorder in graphitic materials [23]. The evaporated OLC displays a ratio of  $D$  band to  $G$  band intensity ( $I_D/I_G$ ) of 0.95, the relative strength of the  $D$  band implies that the OLC particles are highly defective in accord with the HRTEM and XPS data, although the nature of the defects associated with the graphite  $D$  band is a matter of debate [24, 25]. Similarly, the full width at half maximum (FWHM) of the  $D$  band of  $77\text{ cm}^{-1}$  is rather large, providing further evidence of the defective nature of the evaporated OLC particles. The centre of the

(broad)  $G$  band in the evaporated OLC is at  $1590\text{ cm}^{-1}$ , which is identical to that observed by Obraztsova *et al.* [21] for nanodiamond partially graphitized at 1400 K. The position and width (FWHM of  $65\text{ cm}^{-1}$ ) of the  $G$  band, which is in contrast to that for well-graphitized OLC [26], is again indicative of a high degree of structural disorder in the OLC shells.

Nanocrystalline diamond has a relatively narrow Raman band at  $\sim 1323\text{ cm}^{-1}$  [21] and although this overlaps with the  $D$  band in the evaporated OLC sample, shown in Fig. 4, the symmetric shape of the latter suggests that any nanodiamond contribution to the Raman spectrum, if present, is extremely small. Ultra-dispersed nanodiamond samples annealed to the range of temperatures used for evaporation in this study typically form buckydiamonds with a clear contribution from nanodiamond present in the Raman spectra [21]. Only the smallest OLC particles (typically less than about 2 nm in diameter, corresponding to three to five carbon shells) formed by annealing nanodiamond at these temperatures have been observed to have diamond-free cores [21]. Moreover, partially graphitized nanodiamond particles formed in this temperature range are often linked by extended curved graphitic layers [11]. Therefore, we suggest that the absence of an appreciable signal from a nanodiamond core in the Raman spectrum of Fig. 4, the absence of an  $sp^3$ -related signal in XPS and the observation of isolated particles and small agglomerates by AFM (Fig. 2) indicate that the OLC observed in our experiment is either formed from carbon vapor evaporated onto the silicon substrates or by the direct sublimation of only the smallest ( $< 2\text{ nm}$  diameter) OLC particles formed during nanodiamond graphitization. HRTEM images of the material left in the tantalum evaporator after the experiments clearly show OLC agglomerates, some containing ND, which confirms transformation



of much of the ND to OLC aggregates (Fig. 5). It is therefore possible that weakly bound OLC particles could evaporate onto the silicon substrate. We believe that direct sublimation is more likely, considering that the temperatures used in this study are insufficient to yield a significant carbon vapor pressure from the source. However, it is not possible to completely rule out OLC growth by condensation of carbon vapor and further work is needed to resolve this issue.

#### 4. Conclusions

The growth of OLC on silicon by evaporation of material from a nanodiamond source has been studied using XPS, Raman spectroscopy, AFM and HRTEM. This method provides a straightforward method of producing individual, separated OLC nanoparticles. Raman and XPS measurements indicate the presence of  $sp^2$  hybridized carbon, corresponding to OLC and the presence of curved graphitic shells and individual quasi-spherical nanoparticles is demonstrated by HRTEM and AFM. Whilst HRTEM and AFM are spatially localized techniques, XPS and Raman spectroscopy average over a macroscopic area of the film and the agreement between the results of these techniques indicates that a nanodiamond source can be successfully employed to produce uniform films of onion-like carbon particles, although the individual particles are rather defective. The absence of features associated with nanodiamond in Raman spectra or XPS from the evaporated films suggests that the OLC is either formed *in situ* from carbon vapor originating from the nanodiamond containing evaporation source or originates from sublimation of the smallest particles formed by graphitization of the nanodiamond during source heating. Considering the temperatures used in the evaporation process, the second mechanism seems more likely.

## References

- [1] Iijima S. Direct observation of tetrahedral bonding in graphitized carbon-black by high resolution electron-microscopy. *J Cryst Growth* 1980; 50: 675-83.
- [2] Ugarte D. Curling and closure of graphitic networks under electron-beam irradiation. *Nature* 1992; 359 : 707-09.
- [3] Hirata A, Igarashi M, Kaito T. Study on solid lubricant properties of carbon onions produced by heat treatment of diamond clusters or particles. *Tribology International* 2004; 37: 899-905.
- [4] Wu G, Dai CS, Wang DL, Li DY, Li N. Nitrogen-doped magnetic onion-like carbon as support for Pt particles in a hybrid cathode catalyst for fuel cells. *J Mater Chem* 2010; 20:3059-68.
- [5] Pech D, Brunet M, Durou H, Huang PH, Mochalin V, Gogotsi Y, Taberna PL, Simon P. Ultrahigh-power micrometere-sized supercapacitors based on onion-like carbon. *Nature Nano*2010; 5:651-54.
- [6] Gao W, Singh N, Song L, Liu Z, Reddy ALM, Ci LJ, et al. Direct laser writing of micro-supercapacitors on hydrated graphite oxide films. *Nature Nano* 2011;6: 496 – 500.
- [7] Brieva AC, Jager AC, Huisken F, Šiller L, Butenko YV. A sensible route to covalent functionalization of carbon nanoparticles with aromatic compounds. *Carbon* 2009;47: 2812 – 20.
- [8] Gorelik T, Urban S, Falk F, Kaiser U, Glatzel U. Carbon onions produced by laser irradiation of amorphous silicon carbide. *Chem Phys Lett* 2003;373:642- 45.
- [9] Kuznetsov VL, Chuvilin AL, Butenko YV, Mal'kov IY, Titov VM, Onion-like carbon from ultra-disperse diamond. *Chem Phys Lett* 1994;222: 343 -48.

- [10] Kuznetsov VL, Butenko YV, Ch.13, *Diamond Phase Transitions at Nanoscale in Ultrananocrystalline diamond: synthesis, properties, and applications*; O. A. Shenderova and D. M. Gruen (eds), William Andrew Publishing, (2006)
- [11] Butenko YV, Krishnamurthy S, Chakraborty AK, Kuznetsov VL, Dhanak VR, Hunt MRC, Šiller L. Photoemission study of onionlike carbons produced by annealing nanodiamonds. *Phys Rev B* 2005;71: 075420.
- [12] Cabioch T, Riviere JP, Delafond J. A new technique for fullerene onion formation. *J Mater Sci* 1995;30: 4787-92.
- [13] Bruhwiler PA, Maxwell AJ, Puglia C, Nilsson A, Andersson S, Martensson M.  $\pi^*$  and  $\sigma^*$  excitons in C1s absorption of graphite. *Phys Rev Lett* 1995; 74; 614-17.
- [14] Wu YY, Liu JF, Sun B, Liu ZL, Xu PS. Carbonization process and SiC formation at C<sub>60</sub>/Si(111) interface studied by SRPES. *Journal of Physics: Conference Series* 2008; 100: 042039.
- [15] Schmidt J, Hunt MRC, Miao P, Palmer RE. Film growth and surface reactions of C<sub>60</sub> on Si(100)H(2x1). *Phys Rev B* 1997; 56: 9918 - 9924.
- [16] Hunt MRC. Temperature dependence of the electronic and vibrational excitations of C<sub>60</sub> adsorbed on Si(100)-2x1. *J Phys Cond. Mat* 1996;14: L229-35.
- [17] Hunt MRC, Montalti M, Chao Y, Krishnamurthy S, Dhanak VR, Šiller L. Thermally induced decomposition of single-wall carbon nanotubes adsorbed on H/Si(111). *Appl Phys Lett*. 2002; 81: 4847- 49.
- [18] Montalti M, Krishnamurthy S, Chao Y, Butenko YV, Kuznetsov VL, Dhanak VR, Hunt MRC, Šiller L. Photoemission spectroscopy of clean and potassium-intercalated carbon onions. *Phys Rev B* 2003;67: 113401.
- [19] Brzhezinskaya MM, Baitinger EM, and Shnitov VV.  $\pi$ -plasmons in ion-irradiated multiwall carbon nanotubes. *Physica B* 2004;348: 95-100.

- [20] Chakraborty AK, Woolley RAJ, Butenko YV, Dhanak VR, Šiller L, Hunt MRC. A photoelectron spectroscopy study of ion-irradiation induced defects in single-wall carbon nanotubes. *Carbon* 2007;45: 2744-50.
- [21] Obraztsova ED, Fujii M, Hayashi S, Kuzentsov VL, Butenko YV, Chuvilin AL. Raman identification of onion-like carbon. *Carbon* 1998;36: 821 – 26.
- [22] Sano N, Wang H, Alexandrou I, Chhowalla M, Teo KBK, Amaratunga GAJ. Properties of carbon onions produced by an arc discharge in water. *J Appl Phys* 2002;92:2783-88.
- [23] Pimenta MA, Dresselhaus G, Dresselhaus MS, Cançado LG, Jorio A, Saito R. Studying disorder in graphite-based systems by Raman spectroscopy, *Phys Chem Chem Phys* 2007;9:1276-1291.
- [24] Wilhelm H, Lelaurain M, McRae E, Humbert B. Raman spectroscopic studies on well-defined carbonaceous materials of strong two-dimensional character. *J Appl Phys* 1998; 84: 6552 – 88.
- [25] Matthews MJ, Pimenta MA, Dresselhaus G, Dresselhaus MS, Endo M. Origin of dispersive effects of the Raman D band in carbon materials. *Phys Rev B* 1999;59 : R6585-88.
- [26] Lespade P, Aljishi R, Dresselhaus MS. Model for Raman-scattering from incompletely graphitized carbons. *Carbon* 1982;20: 427- 31.

## Figure captions

Figure 1. HRTEM of OLC formed by evaporation onto silicon-coated grids. The arrows indicate the position of the OLC particles. The scale bar corresponds to 5 nm.

Figure 2. AFM image, obtained in tapping mode, of onion like carbon evaporated onto a silicon substrate.

Figure 3. Carbon 1s spectra from onion-like carbon evaporated onto a silicon substrate obtained at normal (solid line) and grazing (dots) emission.

Figure 4. Raman spectra of OLC evaporated on silicon showing *D* and *G* bands.

Figure 5. HRTEM image of the OLC residue remaining in the tantalum evaporator after a deposition cycle.

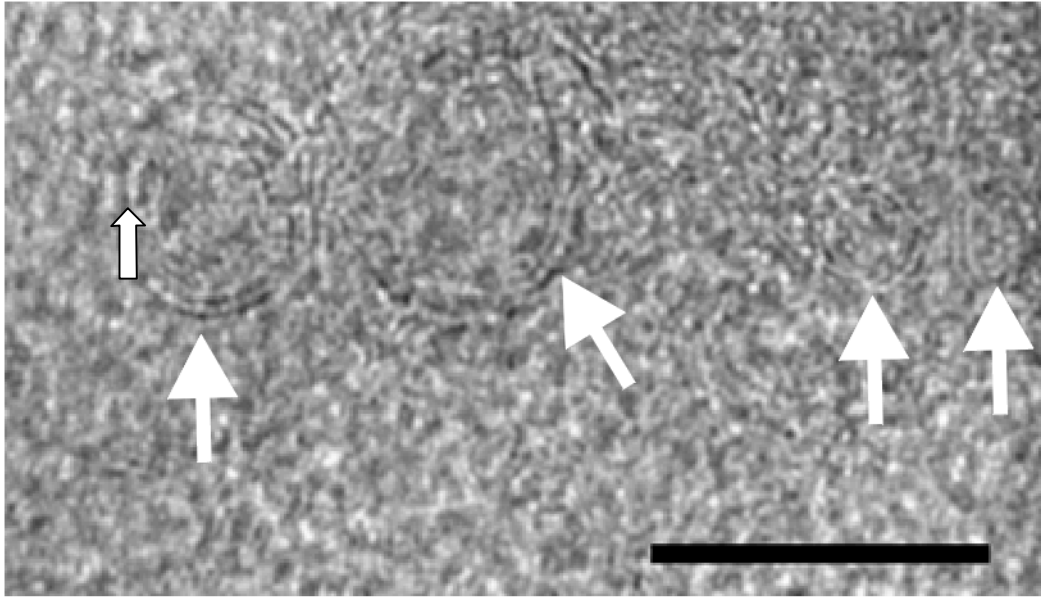


Figure 1

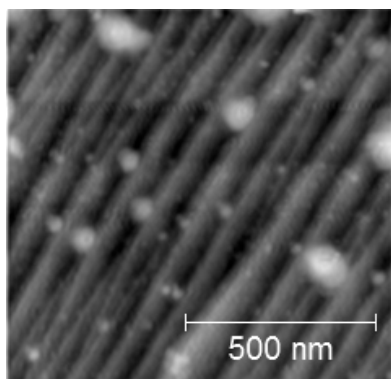


Figure 2

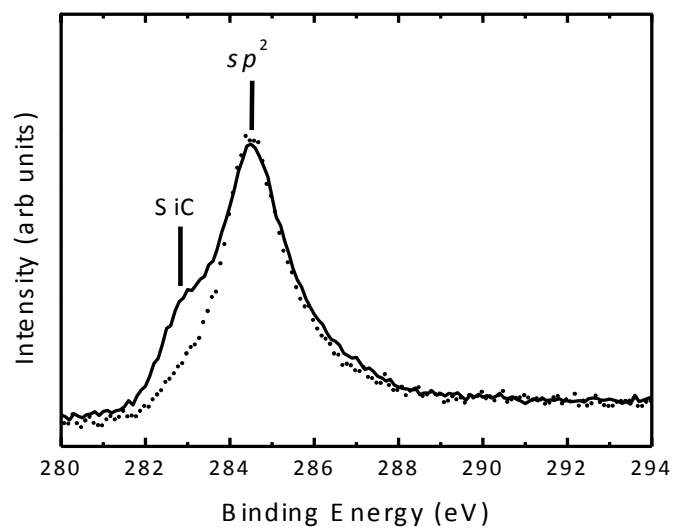


Figure 3



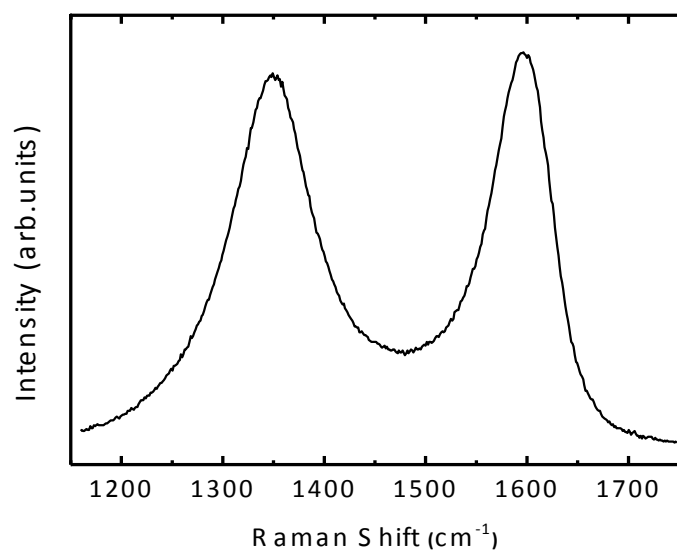


Figure 4

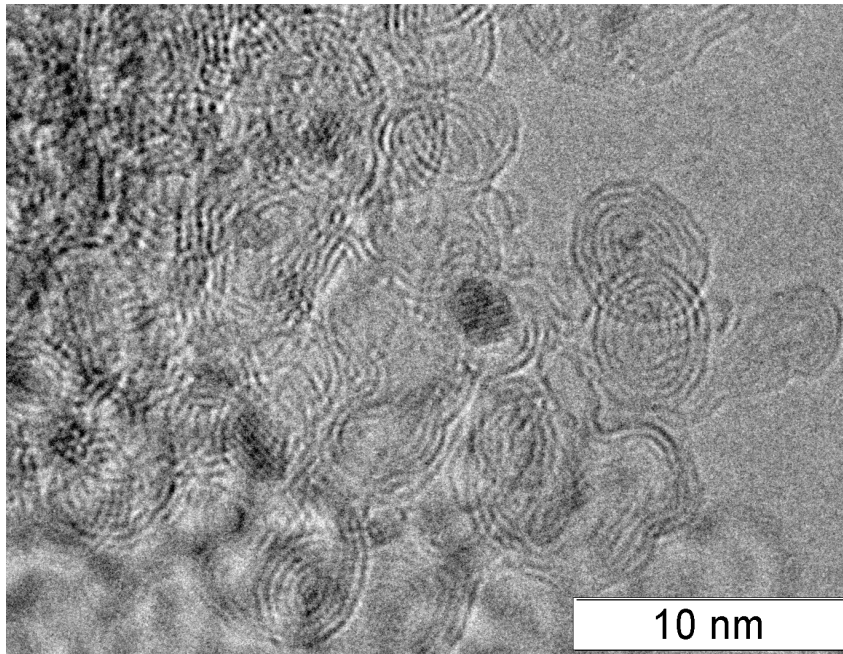


Figure 5